

Dielectric behaviour of ketone-amine binary mixtures at microwave frequencies

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Abstract. Values of dielectric constant (ϵ') and loss factor (ϵ'') have been experimentally determined for binary liquid mixtures of ethyl methyl ketone + ethylenediamine and methyl isobutyl ketone + ethylenediamine at 9.44 GHz microwave frequencies at 30°C. The values of ϵ' and ϵ'' have been used to evaluate the molar polarization, apparent polarization and the excess permittivities. Excess refractive index, viscosity and activation energy of viscous flow have also been estimated. These parameters have been used to explain the formation of 1:1 complexes for both the systems.

Keywords. Polarization; excess parameters; dielectric behaviour; methyl isobutyl ketone binary mixtures.

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1. Introduction

When a binary mixture is formed, the refractive index, viscosity, thermodynamic parameters and dielectric parameters do not vary linearly. The deviation from linearity of these parameters is termed as excess parameters and is helpful to understand the nature of bonding between the two liquids. Recently several workers [1–7] have studied the excess parameters in liquid mixtures.

The nature of complex formation between the molecules may be ascertained by studying apparent molar polarization and is useful in determining the nature of molecular interactions in the liquid systems. In the past, several workers [4, 8, 9] have made dielectric studies of liquid mixtures taking amines as one of the constituent components in the binary mixtures. Govindan and Ravichandran [3] have studied the excess viscosity of ethyl methyl ketone + alcohol mixtures and Das and Swain [2] have studied the methyl isobutyl ketone and monosubstituted benzene mixtures. Dielectric studies of ketone + amine mixtures have not been carried out in the past. As such it was felt that the present studies may provide useful information regarding the molecular interactions and the formation of complexes in the mixtures of ethyl methyl ketone (EMK) + ethylenediamine (EDA) and methyl isobutyl ketone (MIBK) + ethylenediamine (EDA).

2. Experimental details

The dielectric constant (ϵ') and the loss factor (ϵ'') were measured using Surber's [10] technique of measuring the reflection coefficient from the air-dielectric boundary of the

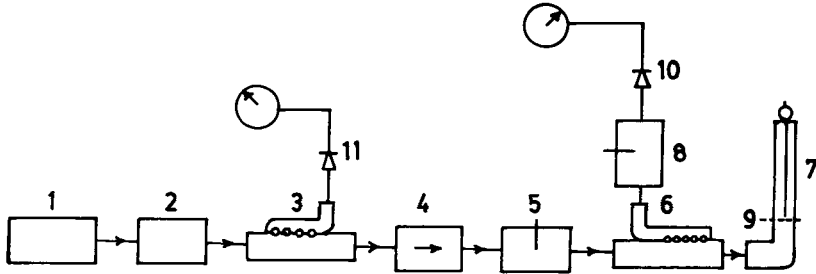


Figure 1. Schematic diagram of the experimental set-up for the measurement of ϵ' and ϵ'' [1, microwave generator; 2, frequency meter; 3 and 6, directional coupler; 4, ferrite isolator; 5 and 8, slide screw tuners; 7, liquid dielectric cell; 9, mica window; 10 and 11, crystal detector and galvanometer].

liquid in the microwave X-band at 9.44 GHz frequency and at 30°C temperature. The experimental set-up is shown in figure 1. The dielectric cell has a movable short. To hold the liquid in the cell, a thin mica window, whose VSWR and the attenuation were neglected, was introduced between the cell and the rest of the microwave bench.

The power loss in dielectric may be expressed as a function of dissipation factor D , defined by

$$D = \frac{\epsilon''}{\epsilon' - (\lambda_0/\lambda_c)^2} = \frac{\tan \delta}{1 - (1/\epsilon')(\lambda_0/\lambda_c)^2} \quad (1)$$

where λ_0 is the free space wavelength and λ_c is the cut-off wavelength for the waveguide.

The propagation constant for the dielectric filled guide may be written as

$$\gamma_d = \alpha_d + j\left(\frac{2\pi}{\lambda_d}\right) \quad (2)$$

where α_d is the attenuation constant due to dielectric and λ_d is the wavelength of the e.m. wave in the waveguide filled with the dielectric. Surber has derived the following relations for the dielectric parameters D , ϵ' and ϵ''

$$D = \tan[2 \tan^{-1}(\alpha_d \lambda_d / 2\pi)] \quad (3)$$

$$\epsilon' = (\lambda_0/\lambda_c)^2 + (\lambda_0/\lambda_d)^2 [1 - \tan^2(\frac{1}{2} \tan^{-1} D)] \quad (4)$$

$$\epsilon'' = \frac{1}{\pi} (\lambda_0/\lambda_d)^2 \alpha_d \lambda_d \quad (5)$$

where $\alpha_d \lambda_d$ is the attenuation per wavelength. Now the parameters to be measured experimentally are λ_d and $\alpha_d \lambda_d$.

In order to determine the above quantities, the movable short of the liquid cell (figure 1) was moved in and out and the corresponding reflection coefficient $|\Gamma|$ was measured by means of the crystal pick-up in the directional coupler. The relationship between the reflected power and the depth of the liquid column is approximately given by a damped sinusoidal wave. The distance between two adjacent minimas of this curve gives $\lambda_d/2$.

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The dissipation factor D for the system may be computed analytically as follows. We define a factor M_n by the relation

$$M_n = |\Gamma_n|^2 / |\Gamma_\infty|^2 = I_n / I_\infty \quad (6)$$

where $n = 1, 2, 3, \dots$, $|\Gamma_n|$ is the reflection coefficient by the liquid column of length $L = n(\lambda_d/2)$ and $|\Gamma_\infty|$ is the reflection coefficient for the liquid column of infinite length. I_n and I_∞ represent corresponding current values.

Let

$$x = \lambda_d / \lambda_g \quad (7)$$

$$y = (1 - x) / (1 + x). \quad (8)$$

According to Surber, attenuation per wavelength is given by

$$\alpha_d \lambda_d = \frac{1}{n} \ln K_1 \{1 + (1 + K_2)^{1/2}\}, \quad (9)$$

where

$$K_1 = \frac{(1 - M_n y^2)}{y(M_n - 1)} \quad (10)$$

and

$$K_2 = \frac{(M_n - 1)(1 - M_n y^4)}{(1 - M_n y^2)^2}. \quad (11)$$

Having determined $\alpha_d \lambda_d$, λ_0 , λ_c and λ_d , the values of parameters D , ε' and ε'' may be calculated by using (3) to (5). The accuracy achieved in the present values of ε' and ε'' are 1 and 5% respectively.

The density and viscosity of the pure components and their mixtures were measured by using the pycnometer and Ostwald's viscometer respectively. The accuracy in the viscosity measurements was estimated to be 0.1%. Refractive indices for sodium D -lines were measured by using Abbe's refractometer having an accuracy up to the third place of decimal.

Ethylenediamine (AG AR grade) supplied by M/s Riedel-Dehaen, Germany was used as such, while ethyl methyl ketone and methyl isobutyl ketone, both AR grade supplied by M/s E Merck, India were used after distillation. The two liquids according to their proportions were mixed well and kept for 4 to 5 h in a well stoppered bottle to ensure good thermal equilibrium.

3. Results and discussion

The values of viscosity (η), square refractive index (n_d^2), dielectric constant (ε'), loss factor (ε''), loss tangent ($\tan \delta$) and activation energy (E_a) for the viscous flow, with increasing mole fraction (X) of EDA for the binary mixtures of EDA + EMK and EDA + MIBK are listed in table 1.

The variation of the dielectric constant (ε') with molar concentration of EDA in the mixture is presented in Figure 2. A pronounced minimum is observed in the curve at $X = 0.63$ for the EDA + EMK system and at $X = 0.74$ for the EDA + MIBK binary system, which indicates the formation of complex in these binary mixtures, as observed by Combs *et al* [11] for the alcohol + *o*-dichlorobenzene mixtures.

Table 1. Values of mole fraction (X) of EDA, viscosity (η), square of the refractive index (n_D^2), dielectric constant (ϵ'), dielectric loss (ϵ''), loss tangent ($\tan \delta$) and activation energy (E_a): for the binary liquid systems at 30°C.

X	η (cp)	n_D^2	ϵ'	ϵ''	$\tan \delta$	E_a (Kcal/mole)
system: EDA + EMK						
0.00000	0.403	1.90992	18.217	2.397	0.1316	2.7273
0.13393	0.595	1.98246	14.305	2.951	0.2063	2.9000
0.25599	0.999	2.04204	11.901	3.315	0.2786	3.1922
0.37243	1.870	2.07360	8.911	3.762	0.4222	3.5397
0.48129	3.935	2.11412	8.086	3.828	0.4734	3.9532
0.58215	4.519	2.12285	7.636	3.883	0.5085	4.0174
0.62827	4.078	2.12576	7.089	3.911	0.5518	3.9511
0.76277	2.974	2.12868	9.803	4.821	0.4918	3.7518
0.84674	2.374	2.13014	11.134	5.255	0.4720	3.6081
0.92485	2.126	2.13160	12.859	5.904	0.4591	3.5352
1.00000	1.653	2.13452	14.504	6.221	0.4565	3.3760
system: EDA + MIBK						
0.00000	0.487	1.95720	11.671	4.799	0.4112	3.0390
0.17450	0.701	1.99092	10.993	5.017	0.4564	3.2072
0.34525	1.066	2.02493	10.613	5.109	0.4814	3.3875
0.44962	1.347	2.04776	10.427	5.212	0.4998	3.4895
0.58440	1.940	2.07360	10.356	5.222	0.5042	3.6560
0.65548	2.099	2.09670	10.100	5.240	0.5188	3.6678
0.74085	2.499	2.11994	8.868	5.344	0.6026	3.7426
0.81642	2.379	2.12576	10.124	5.577	0.5508	3.6799
0.89379	1.899	2.12868	11.142	5.749	0.5160	3.5098
0.94979	1.815	2.1316	12.538	5.921	0.4723	3.4558
1.00000	1.653	2.13452	14.504	6.621	0.4565	3.3760

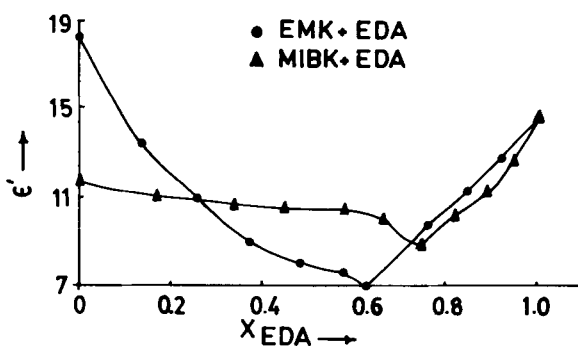


Figure 2. Variation of ϵ' versus mole fraction of EDA in the mixture.

Microwave absorption

It is seen from figure 3, that the absorption in the mixture is greater than that in pure liquids, a maxima in the $\tan \delta$ curve occurring at 0.63 and 0.74 mole fraction of EDA in

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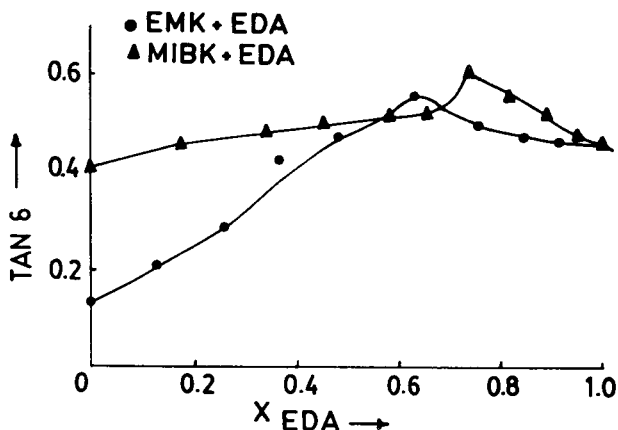


Figure 3. Variation of $\tan \delta$ versus mole fraction of EDA in the mixture.

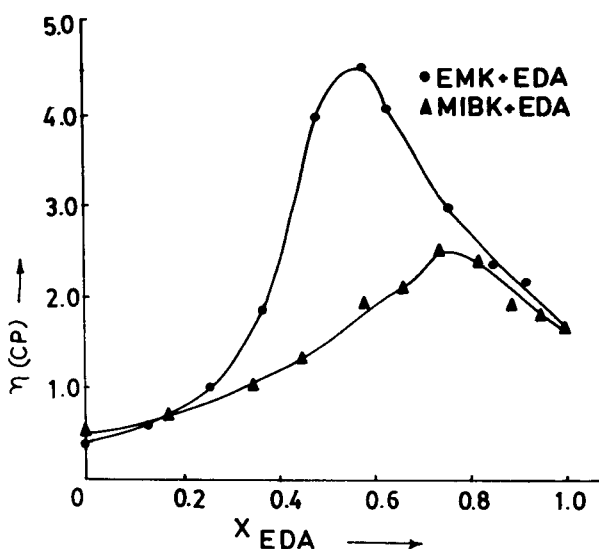


Figure 4. Variation of viscosity of the mixture versus mole fraction of EDA in the mixture.

the EDA + EMK and EDA + MIBK mixtures respectively. We may explain this, by considering the Debye's equation [12] for $\tan \delta$ for a dilute solution of a polar liquid in a non-polar solvent

$$\tan \delta = \frac{(\epsilon' + 2)^2}{\epsilon'} \cdot \frac{4\pi \times N\mu^2}{27KT} \cdot \frac{\omega\tau}{(1 + \omega^2\tau^2)} \quad (12)$$

This equation suggests that the absorption will increase, if the dipole moment μ and relaxation time τ increase. Assuming the approximate validity of the Debye's equation

to our case, the formation of the complex will increase the dielectric absorption due to the following considerations.

In the complex, the dipole moment can be taken as $(\mu_1 + \mu_2)$, μ_1 and μ_2 being the dipole moments of the constituent molecules. For n molecules of each liquid forming the complex, the absorption would be proportional to $n(\mu_1^2 + \mu_2^2)$ for pure liquids, assuming no interaction. On the other hand, in the mixture the absorption would be proportional to the greater term $n(\mu_1 + \mu_2)^2$.

Regarding the role of τ , it is reasonable to assume that at microwave frequencies $\omega\tau < 1$ and due to the larger size of the complex molecules, τ is expected to increase and so would the term $\omega\tau/(1 + \omega^2\tau^2)$ leading to increase of absorption.

Maxima in the viscosity curve

When the viscosity (η) is plotted against mole fraction, the curve shows a sharp maximum (figure 4). The maxima for the EDA + EMK mixture occurs at 0.58 mole fraction of EDA and for EDA + MIBK mixture it occurs at 0.75 mole fraction of EDA. The maxima for the EMK is much pronounced than that for MIBK. Huyskens *et al* [9] have explained the increase in η for the acid amine and phenol-amine mixtures due to the formation of dissociated ions in the mixtures. which is exothermic and depends upon the acidic strength of phenol. Since in the present case EMK reacts with EDA by an exothermic reaction, the pronounced maxima for the EMK may be associated with the formation of dissociated ions in the mixture and due to the more acidic character of EMK than MIBK. The spectacular increase in η may also be attributed to the mutual viscosity of the ketone and amine molecules, as provided by the Andrade's [13] theory.

Molar and apparent polarizations

The values of polarization of the mixtures were obtained using the formula

$$\frac{\epsilon' - 1}{\epsilon' + 2} \cdot \frac{X_1 M_1 + X_2 M_2}{d} = P_{12} \quad (13)$$

where M_1 and M_2 are the molecular weights; X_1 and X_2 the molar concentrations of the constituents of the mixture; and d the density of the mixture. Then following Earp and Glasstone [14] and assuming the formula

$$P_{12} = X_1 P_1 + X_2 P_2 \quad (14)$$

(where P_2 is the apparent polarization of each liquid in the mixture, if P_1 is the polarization of the other component of the mixture in the pure liquid state); values of P_1 and P_2 were calculated. The values of molar polarization P_{12} are plotted in figure 5, as a function of mole fraction of EDA in the mixture.

In the present investigation of ketone-amine mixtures, the amount of complex present is responsible for the shape of our polarization curves and the minimum in the curve is caused by the presence of a complex (or complexes). We may determine the presence of a maximum mole per cent complex by the method earlier used by Combs *et al* [11]. We may assume that a single complex is formed in the complexation reaction



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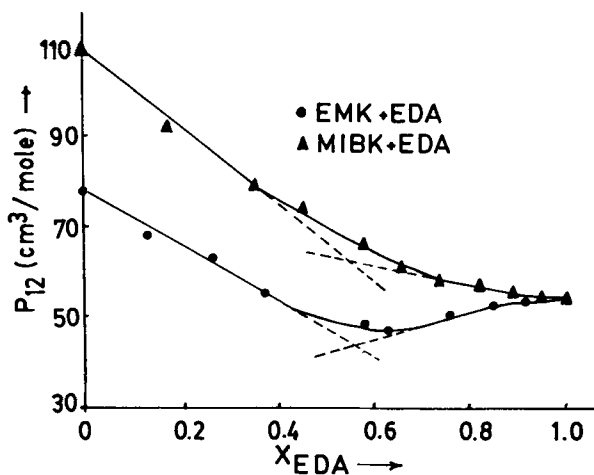


Figure 5. Variation of molar polarization versus mole fraction of EDA in the mixture.

where A represents the ketone, B represents the EDA and C represents the complex. On imposing the extremum condition $d[C]/dx = 0$, we obtain the relationship

$$n = x/(1 - x) \quad (16)$$

where x is the mole fraction of B at the extremum.

We may interpret figure 5 as representing two regions (high and low EDA concentrations), the intersection of the straight lines representing these separate regions can be interpreted as ideally representing the point of maximum concentration of complex. The value of X_{EDA} at this point may then be used in the above equation to determine n . The point of intersection for both the systems occurs at about 0.55 X_{EDA} which corresponds to a 1:1 complex for both the systems and this reflects the acidic character of EMK and MIBK. The acidic character of ketones may be attributed by the enolization of the carbonyl group. Thus these results regarding the formation of complex are supported by our earlier conclusions made from the ϵ' versus mole fraction and $\tan \delta$ versus mole fraction curves for both the systems under investigation.

The values of the apparent polarization for EMK and MIBK are presented as a function of mole fraction of ketone in figure 6. The flat portion of these curves clearly indicates the formation of complex in the ketone + amine mixtures. The more pronounced the flat portion, the more stable is the complex. This indicates that the complex formed with MIBK is more stable than the complex formed with the EMK. Similar results have been obtained by Combs *et al* [11] for the alcohol + *o*-dichlorobenzene mixtures.

Excess parameters

The excess values of permittivity $\Delta\epsilon'$, $\Delta\epsilon''$, excess viscosity $\Delta\eta$, excess square refractive index Δn_D^2 and excess activation energy ΔE_a for both the systems are presented in

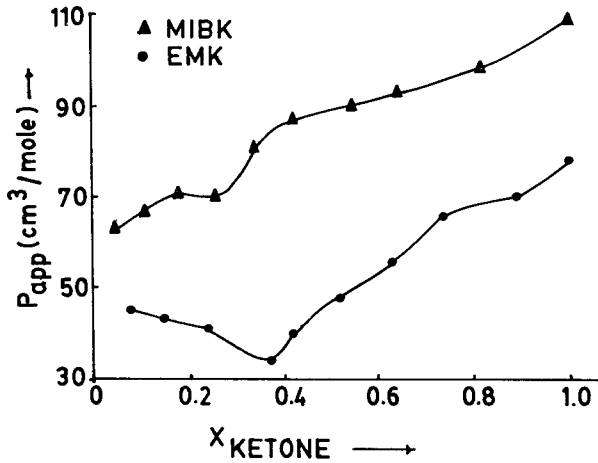


Figure 6. Variation of apparent polarization versus mole fraction of ketone in the mixture.

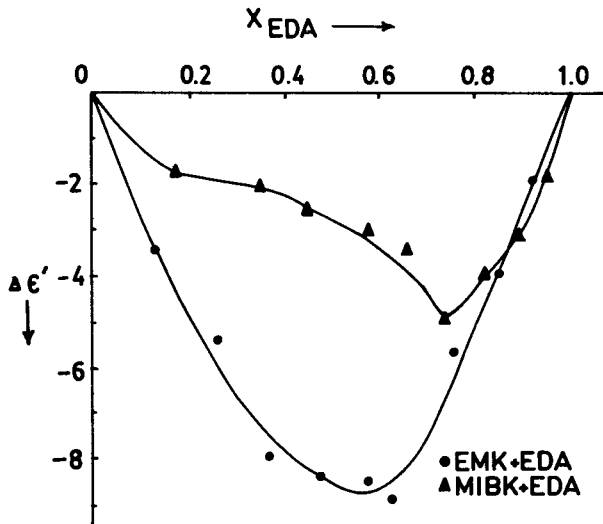


Figure 7. Variation of excess permittivity versus mole fraction of EDA in the mixture.

figures 7 to 11. The excess values were then calculated by using the relations of the form

$$\Delta Y = Y_m - (X_1 Y_1 + X_2 Y_2) \quad (17)$$

where ΔY is any excess parameter and Y refers to the above mentioned quantities. The subscripts $m, 1$ and 2 used in the above equation are respectively for the mixture, component 1 and component 2. X_1 and X_2 are the mole fractions of the two components in the liquid mixtures.

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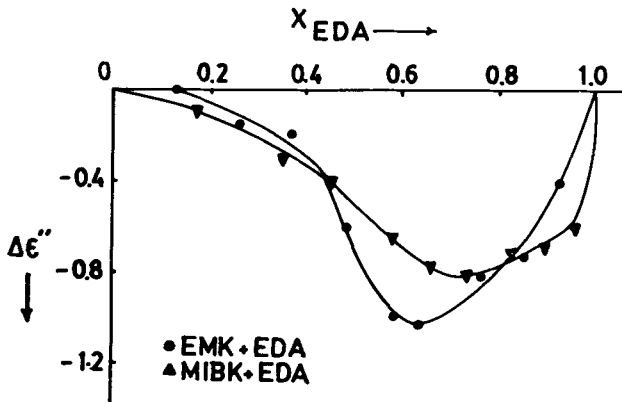


Figure 8. Variation of excess loss factor versus mole fraction of EDA in the mixture.

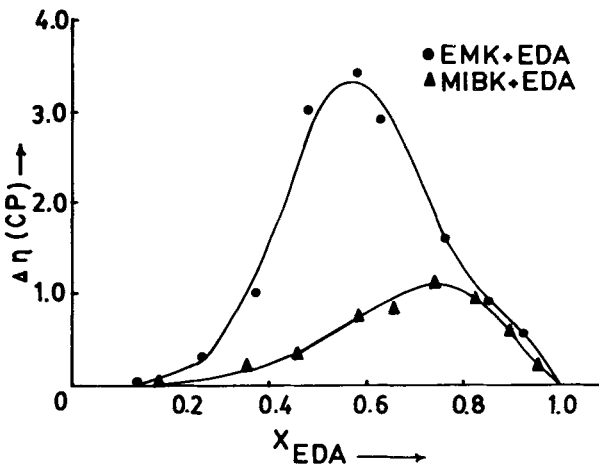


Figure 9. Variation of excess viscosity versus mole fraction of EDA in the mixture.

The free energy of activation E_a of the viscous flow for the pure liquid and their liquid mixtures is obtained by using the relation

$$\eta = \frac{hN}{V} \exp(E_a/RT) \quad (18)$$

where η and V are the viscosity and the molar volume of the liquids respectively and other symbols have their usual meaning.

The excess values were fitted through least squares with all points equally weighted by using the Redlich-Kister [15] equation,

$$\Delta Y = X_1 X_2 \sum_j A_j (X_1 - X_2)^j \quad (19)$$

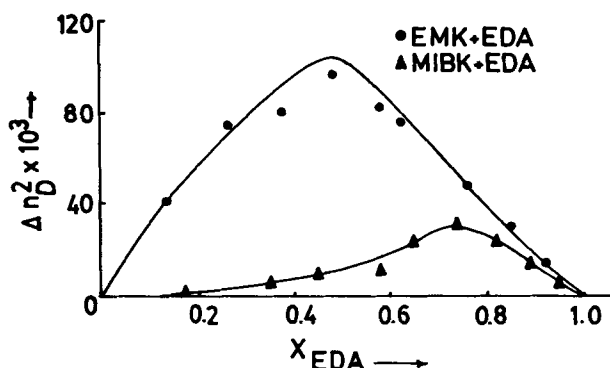


Figure 10. Variation of excess square refractive index versus mole fraction of EDA in the mixture.

Table 2. Values of coefficients A_j 's and standard deviations (σ) in various excess parameters for the two binary liquid systems at 30°C.

Physical parameter (ΔY)	A_0	A_1	A_2	A_3	A_4	A_5	σ
system: EDA + EMK							
$\Delta\epsilon'$	-33.56	-11.96	-3.07	54.58	23.70	-61.45	2.3780
$\Delta\epsilon''$	-2.37	-7.73	-1.34	17.91	2.87	-18.30	0.3646
$\Delta\eta$	11.69	14.84	-37.38	-24.45	41.59	9.43	1.1876
Δn_D^2	0.51	-0.29	-1.34	1.35	1.76	1.88	0.0260
ΔE_a	3564	2171	-7105	-3297	6626	2905	292.50
system; EDA + MIBK							
$\Delta\epsilon'$	-10.64	-12.35	-22.85	-1.01	2.58	2.91	0.9826
$\Delta\epsilon''$	-2.15	-4.60	-1.82	15.03	0.78	-27.54	0.5075
$\Delta\eta$	2.05	5.09	3.21	6.09	-0.39	-14.96	0.3700
Δn_D^2	0.05	0.12	0.11	0.11	-0.04	-0.31	0.0090
ΔE_a	1436	1748	361	-1288	-455	-320	129

where Y is any physical parameter and X_1 and X_2 are the concentrations of the two constituents. Buep and Baron [7] have used three coefficients (from $j = 0$ to 2) and Fattepur *et al* [1,4] have used five coefficients (from $j = 0$ to 4) in this equation. However, the fitting achieved was not perfect in all the cases. It was therefore observed that if we take more terms in the expansion and solve these equations by the method of least squares, better curve fitting may be achieved. Therefore we chose six coefficients in the expansion. The values of coefficients A_j 's for $j = 0$ to 5 are given in table 2 along with the standard deviation σ . By using these A_j values, excess parameters (ΔY) calculated are used as guidelines to draw smooth curves in figures 7 to 11. It has been observed that the present fitting is better and the present values of the excess parameters show deviations only up to 5% from the experimental data.

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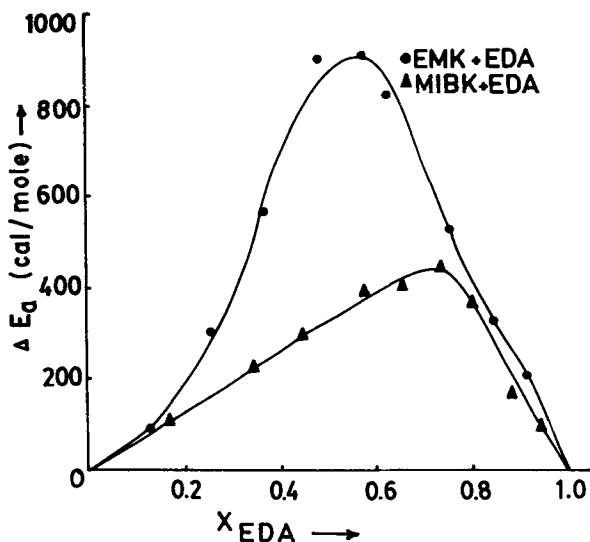


Figure 11. Variation of excess activation energy versus mole fraction of EDA in the mixture.

The excess permittivity ($\Delta\epsilon'$) and excess loss ($\Delta\epsilon''$) are negative for both the ketone-amine mixtures. The minima in the $\Delta\epsilon'$ and $\Delta\epsilon''$ curves for the EDA + EMK mixture occur at 0.58 and 0.63 mole fraction of EDA respectively, which are close to the value of mole fraction of EDA at which we expect the formation of complexes on the basis of ϵ' , $\tan \delta$ and η curves given in figures from 2 to 4. Similarly for the MIBK + EDA mixture the minima in the $\Delta\epsilon'$ and $\Delta\epsilon''$ curves occur at 0.74 mole fraction of EDA, which supports our earlier conclusion of the complex formation based on figures 2 to 4. The excess dielectric permittivity is associated with the polarization and loss is regarded due to the molecular motions which are governed by the complex forces of molecular interactions. Thus the excess loss may be regarded as a parameter which reflects the entropy change in a binary system.

The excess viscosity, square refractive index and activation energy are all positive, indicating strong interactions between the ketone and amine molecules. For all these excess parameters the maxima for the EMK + EDA mixture occurs at about 0.55 mole fraction of EDA and for MIBK + EDA mixture maximas occurs at about 0.75 mole fraction of EDA. The values of dipole moment μ obtained [16, 17] for EMK and MIBK are 3.13 Debye and 2.55 Debye respectively. The higher μ value of EMK indicates that the dipole-dipole interactions in EMK are stronger than MIBK. This behaviour of EMK is supported by the higher values of activation energy and excess activation energy of EMK as compared to MIBK. The deviation of excess activation energy of viscous flow in these systems indicate the increase in the internal energy of the viscous flow, thus supporting the presence of strong interactions in the systems of ketone and amines.

4. Conclusions

The molar polarization, apparent polarization and excess dielectric parameters have been reported for EMK + EDA and MIBK + EDA binary mixtures at various concentrations. These studies suggest the strong interactions between the ketone and amine molecules. The molar polarization curves suggest the formation of 1 : 1 complexes in the mixtures of EMK + EDA and MIBK + EDA systems. The pronounced peaks in the viscosity and excess parameter curves suggest the more acidic character of EMK than MIBK.

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